

## NEGATIVE ELECTRON AFFINITY EFFECT ON THE SURFACE OF CHEMICAL VAPOR DEPOSITED DIAMOND POLYCRYSTALLINE FILMS.

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### ABSTRACT

Strong negative electron affinity effects have been observed on the surface of as-grown chemical vapor deposited diamond using Secondary Electron Emission. The test samples were randomly oriented and the surface was terminated with hydrogen. The effect appears as an intensive peak in the low energy part of the spectrum of the electron energy distribution and may be described in the model of effective negative electron affinity.

One of the remarkable features of diamond is the negative electron affinity (NEA) that may be observed on its surface under specific conditions.<sup>1-10</sup> For NEA the vacuum energy level lies below the conduction band minimum which allows electrons to escape easily from the surface.<sup>11</sup> Semiconductors with NEA are widely used as photo- and cold-cathode emitters.

NEA from diamond has been shown to correspond with the presence of hydrogen bounded to the surface.<sup>1-5</sup> Special surface treatment of single crystal diamond and epitaxial films is, therefore, usually necessary to activate NEA. Recently, chemical vapor deposited (CVD) polycrystalline diamond films have received a great deal of attention because they are promising for novel electronic applications due to their additional advantages in comparison with diamond single crystals. Their fabrication is relatively easier and cheaper, they can be grown with high levels of impurity doping, and they can have correspondingly high conductivity.<sup>12</sup> CVD diamond has also been observed to display high secondary electron emission (SEE) properties. Total

secondary yield coefficients,  $\sigma=12-50$ , have been measured from such films terminated with hydrogen,<sup>13-16</sup> which is indirect evidence of a strong NEA effect in this material.

In this Letter we present a direct proof of the NEA effect on the surface of as-grown CVD randomly oriented polycrystalline diamond films.

Since the pioneer work<sup>1</sup> a commonplace tool for determination of the presence of NEA in diamond has been the method of ultraviolet photoemission electron spectroscopy (UPS). The idea behind the measurement is very simple. Hot photoelectrons photoexcited to the conduction band cool in the process of energy relaxation and accumulate in the conduction band minimum. At an NEA surface these electrons can be emitted into the vacuum without any energy barrier and appear in photoemission spectra as a sharp peak at low electron energies. Obviously, the existence of the same kind of peak should be expected at the low energy edge of the SEE spectra under excitation of an NEA surface with a beam of primary electrons.

In this study, we use SEE spectroscopy to find a NEA phenomenon in CVD randomly oriented polycrystalline films. The samples were made by depositing 10-20  $\mu\text{m}$  continuous films on Mo substrates by microwave-plasma CVD. During the deposition process, the films were heavily doped with B up to a concentration of about  $10^{20} \text{ cm}^{-3}$ . Experiments were conducted in an ultra high vacuum chamber with a base pressure of  $2 \times 10^{-10}$  torr. Energy distributions of the secondary electrons were measured with a single pass (Perkin Elmer) CMA auger analyzer. Samples were biased at  $V_t = -1.5$  to  $-5$  V, where  $V_t$  is the bias voltage of the target, during the measurements to compensate the workfunction difference between the target and the analyzer and to make the measurements of the low energy region of the spectrum more reliable.

Fig.1 shows the low energy part of the secondary electron spectra of an as-grown CVD

diamond polycrystalline film as a function of energy  $E = e (V_a - V_i)$  ( where  $V_a$  is the analyzer sweep voltage ). For this sample  $\sigma = 35$  measured with a primary beam of energy  $E_p = 3$  keV. It can be seen that most of the secondary electrons are collected in the form of a sharp low energy peak with maximum position at  $E_{\text{max}} = (0.5 - 0.6)$  eV and with  $(0.6 - 0.7)$  eV full width at half maximum (FWHM). The shape of the energy distribution curves and the peak positions had very little dependence on the sample bias in the measured range. Therefore, we can conclude that there were no significant instrumental distortions of the true electron spectrum in our experiments. Observation of the strong low energy peak in the secondary electron distribution is evidence of the NEA effect in CVD diamond films.

To investigate the role of hydrogen termination on the NEA effect, the influence of beam exposure on the spectrum was studied. Continuous electron beam irradiation of these films is well known to result in desorption of hydrogen from the surface and, in turn, a decrease in the secondary electron yield.<sup>16</sup> Fig.2 demonstrates transformation of the secondary electron spectrum after exposure to the electron beam for up to 6 hours at a current density of  $0.180 \text{ mA/cm}^2$  and  $E_p = 3$  keV. This treatment of the surface led not only to the significant reduction of the value of  $\sigma$  (from 32 to 5) but also to the decrease of the contribution of the low energy peak to the energy distribution (dotted curve). Subsequent exposure of the sample to a molecular hydrogen environment at a pressure of  $5 \times 10^{-6}$  torr for 1 hour restored the primary distribution function of the secondary electrons (dashed curve). Therefore, we observed a direct correlation between hydrogen coverage and NEA effect of the diamond film surface.

The total secondary electron emission yield of the diamond films on Mo was previously observed to increase with an increase in the primary beam energy in the range of  $E_p = 1 - 1.5$

keV and to saturate at the larger beam energies<sup>13-15</sup> In this study we have investigated changes in the SEE spectra versus  $E_p$  and have found that the yield increase was accompanied by the enhancement of the low energy peak magnitude as compared with the rest of the energy distribution curve (see Fig.1). The ratio,  $K$ , of the number of low energy electrons in this peak (the area under the peak) to the total number of secondary electrons (the area under the distribution curve in the measured range up to  $V_a=14$  eV) versus  $E_p$  is shown in Fig.3.

There are two possible ways to describe the NEA phenomenon (Fig.4).<sup>6, 9-11</sup> It can be done in terms of either true or effective negative electron affinity. The effective NEA can be described as a consequence of the depletion band bending at the surface of the semiconductor. This band bending may result in the vacuum energy level occurring at an energy below the minimum of the conduction band.<sup>11</sup> The magnitude of the effective NEA can be defined as  $\chi_{\text{eff}} = \phi_{\text{BB}} - \chi$ , where  $\phi_{\text{BB}}$  is band bending and  $\chi$  is positive electron affinity (Fig.4b). In the case of the true NEA model the semiconductor crystal has negative electron affinity as its intrinsic property (Fig.4a).

Data obtained in this investigation agree with the effective NEA model for CVD diamond films. Indeed, the increase of the efficiency of the low energy electron emission as the primary beam energy is increased (Fig.3) may be easily understood in the model of the effective NEA. The thickness of the depletion layer can be evaluated from the expression<sup>17</sup>  $L_{\text{BB}} = (\phi_{\text{BB}} \kappa / 2\pi e N_A)^{1/2} \approx 25 \text{ \AA}$  for our samples,<sup>18</sup> taking for the estimation  $\phi_{\text{BB}} = 1 \text{ eV}$ , dielectric constant  $\kappa=5$  and  $N_A \approx 10^{20} \text{ cm}^{-3}$ . The mean free path of electrons with  $E_p < 1 \text{ keV}$  in solids does not exceed 20 -30  $\text{\AA}$  and excitation of the secondary electrons occurs mostly in the surface depletion layer, from where the large number of the low energy electrons can not escape due to the existence of a

potential barrier. At  $E_p > 1.5$  keV the secondary electrons are excited below the depletion layer and the low energy electrons can freely escape into the vacuum from the bulk conduction band. Therefore, the contribution of the very low energy electrons into the energy distribution spectrum increases sharply with the increase of the primary beam energy. In the case of true NEA it should be expected that relative contribution of the very low energy electrons into the spectrum would not strongly depend on the energy of primary electrons.

We should note also that the onset of the electron spectrum, as seen in Figs.1 and 2, corresponds to secondary electrons having near zero kinetic energy  $E_0$ . It is clear from the band diagram shown in Fig.4 that these electrons can be observed only when the effective NEA condition exists on a surface ( for the true NEA surface minimum kinetic energy of electrons would be equal to  $|\chi - \phi_{BB}|$  ).

It can be seen from Figs.1 and 2 that FWHM of the low energy peak is much larger than  $kT$ . The same peak shape has been observed in all photoemission measurements independent of the crystal orientation of the surface and its preliminary treatment when samples were excited by photons with energy significantly exceeding the diamond band gap.<sup>1-10</sup> It might be, therefore, that the peak width is associated with the energy distribution of electrons inside the crystal rather than with surface potential fluctuations.<sup>1</sup> A strong nonequilibrium distribution of low energy electrons in the conduction band minimum is produced during the SEE process because their escape time,  $\tau_{esc}$ , is smaller than the energy relaxation time, which is mainly determined by interaction with optical phonons. If the electron energy does not exceed the energy of a few optical phonons this relaxation time can be estimated as  $\tau_e \approx 10^{-12} - 10^{-13}$  s.<sup>19, 20</sup> At the depth of penetration of the primary electrons in the crystal  $l \approx 50$  Å, and velocity of the low energy secondary electrons  $v$

$\approx 10^7 \text{ cm s}^{-1}$ ,  $\tau_{\text{esc}} = 1 / v < 10^{-13} \text{ s}$ . The condition  $\tau_{\text{esc}} < \tau_e$  is fulfilled for all electrons from the peak which has FWHM approximately equal to the energy of four optical phonons in diamond ( $\hbar\omega_{\text{opt}} = 0.163 \text{ eV}$ ). The relaxation time of electrons with energies less than  $\hbar\omega_{\text{opt}}$  is much longer than  $10^{-12} \text{ s}$ . Therefore, we can anticipate that the maximum of the energy distribution of secondary electrons in the conduction band would be at least one energy of an optical phonon above its bottom. Consequently, assuming that the secondary electrons with zero kinetic energy are coming out of the solid at the vacuum level, we can estimate the value of  $\chi_{\text{eff}}$  for the film under investigation as  $\chi_{\text{eff}} \leq (E_{\text{max}} - E_0) - \hbar\omega_{\text{opt}}$ . Using data from Fig.1 and the band diagram ( Fig.4) we obtained  $\chi_{\text{eff}} < 0.4 \text{ eV}$ .

In conclusion, we have found a strong NEA effect on the surface of a randomly oriented CVD polycrystalline diamond film terminated with hydrogen using the SEE spectroscopy method. The effect appears as a strong peak at the low energy part of the electron energy distribution and may be described in the model of effective NEA.

The authors would like to thank Yaxin Wang and John C. Angus of Case Western Reserve University for producing the diamond samples used in the investigation.

This work was supported by the National Research Council and NASA Lewis Research Center.

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- <sup>17</sup> T.Ando, A.Fowler, and F.Stern, *Rev. Mod. Phys.* **54**, 437, (1982)
- <sup>18</sup> The narrow potential well is really a two-dimensional quantum well for electrons . At some ratio between the depth and the width of this nonsymmetrical well bound electron states in it do not exist. In this case the surface with effective NEA transforms into the one with true NEA.
- <sup>19</sup> E.M.Conwell, *High Field Transport in Semiconductors*, (Suppl. 9 to *Sol. St. Phys.* Academic Press, N.Y. ,1967.)
- <sup>20</sup> There is an additional effective mechanism of energy relaxation of hot electrons in heavily p-doped semiconductors: electron - hole scattering. The estimate shows for our samples this relaxation time is also about  $10^{-13}$  s.

## FIGURE CAPTIONS

Fig.1. Energy distributions of secondary electrons  $N(E)$ , for primary energies  $E_p = 200$  eV ( solid curve ), and  $E_p = 1500$  eV ( dashed curve ). Data are normalized to the low energy peak maximum.

Fig.2. Energy distributions of secondary electrons for as-grown diamond film - solid curve, after exposure of the film to the electron beam for up to 6 hours at the current density of  $0.18$  mA/cm<sup>2</sup> and  $E_p = 3$  keV - dotted curve, and after subsequent exposure of the same film to a molecular hydrogen environment at the pressure of  $5 \times 10^{-6}$  Torr for 1 hour - dashed curve. Data are normalized to the low energy peak maximum.

Fig.3. The ratio,  $K$ , of the number of very low energy electrons in the peak of  $N(E)$  to the total number of observed secondary electrons as a function of energy of primary electron beam.

Fig.4. Near the surface band diagram of a semiconductor for (a) true negative affinity and (b) effective negative affinity models.

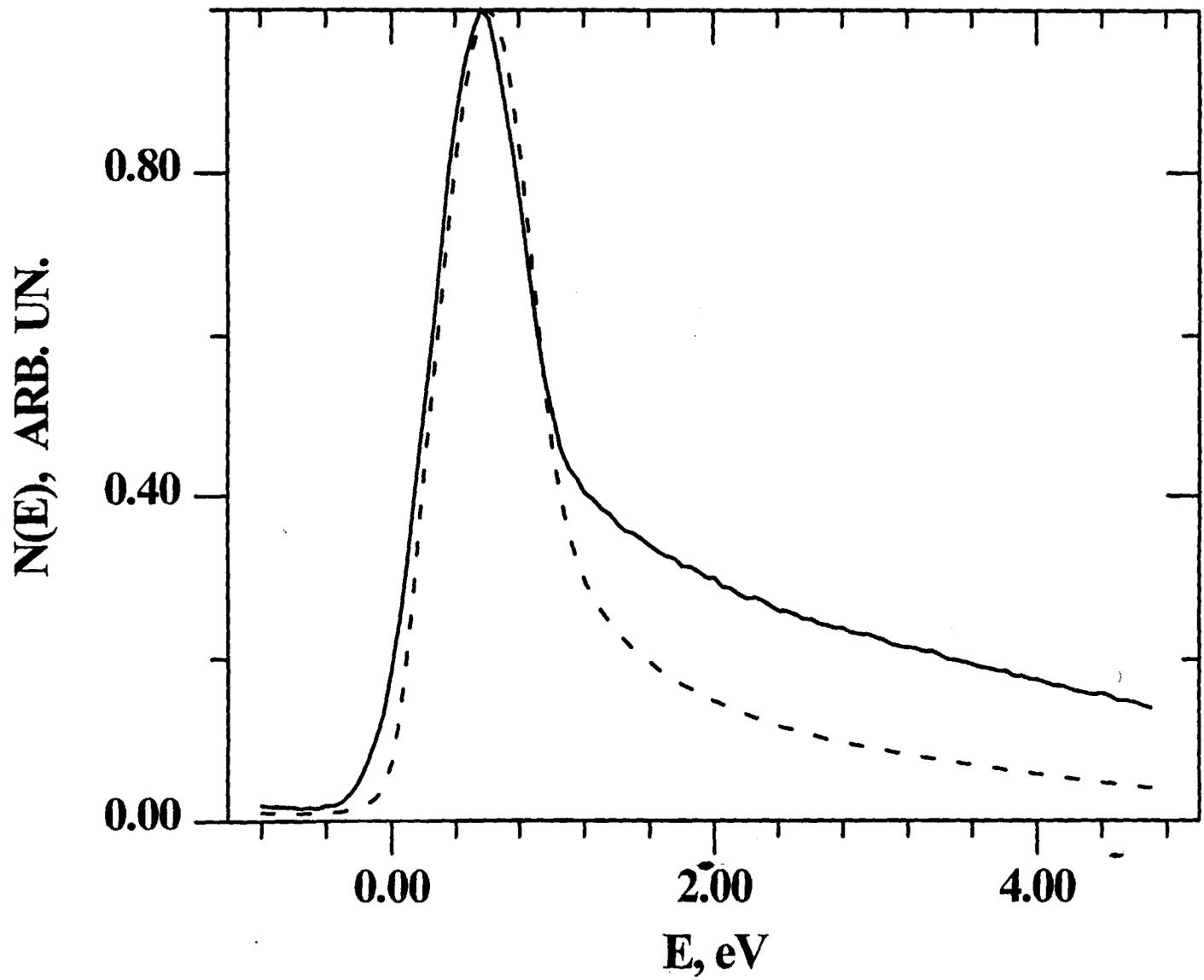


Fig. 1

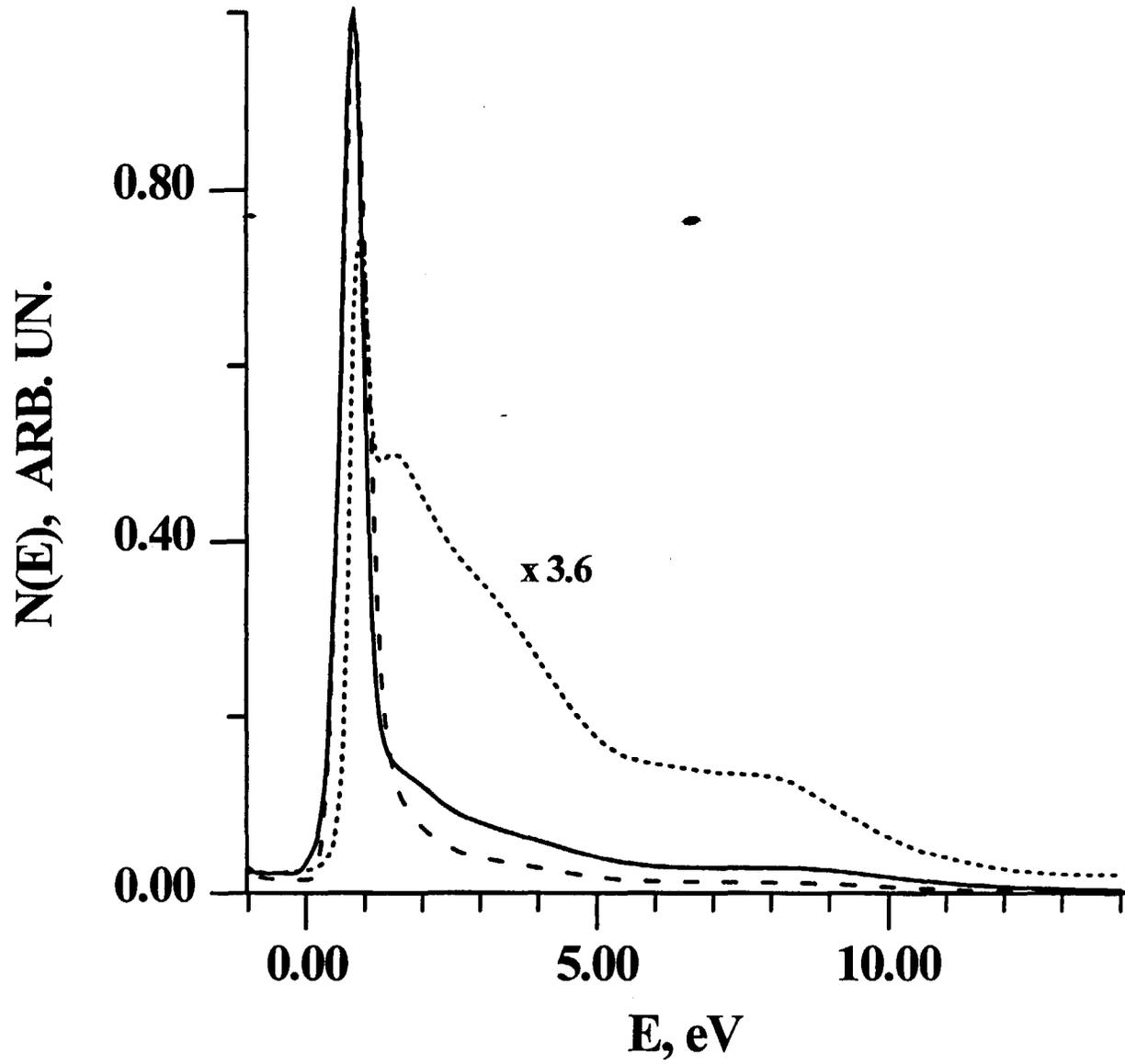
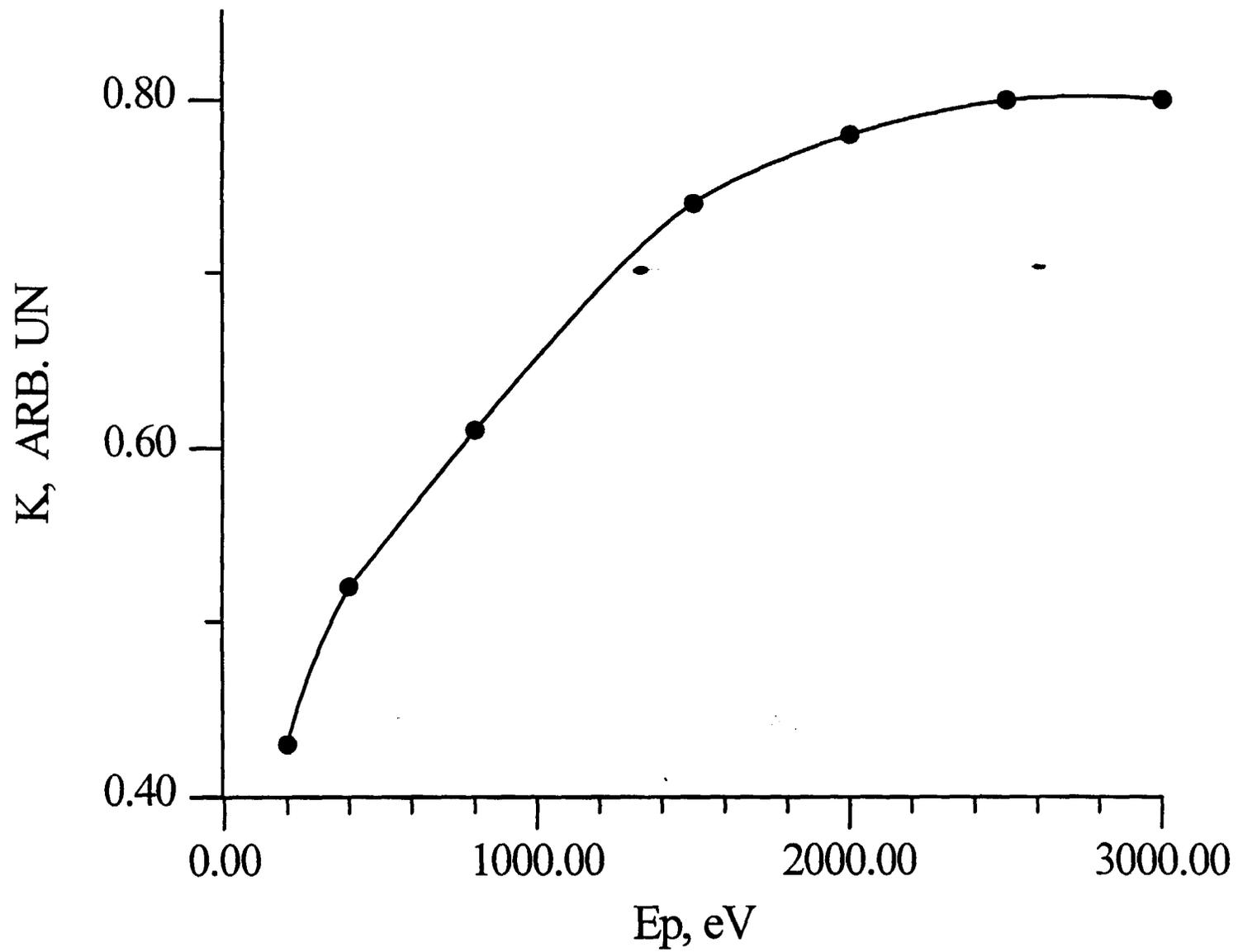
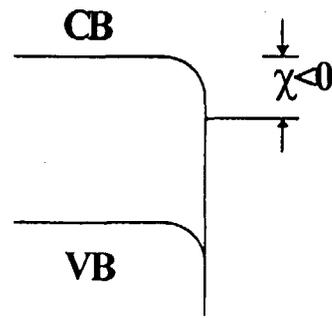


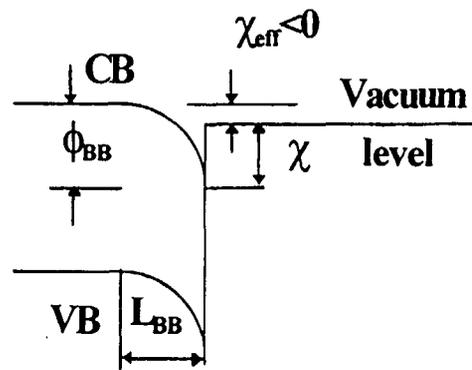
Fig. 2



**Fig. 3**



(a)



(b)

**Fig. 4**